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Application of ultrasound and Fenton's reaction process for the treatment of oily sludge

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Abstract

In this study, three advanced oxidation processes (AOP) were investigated for their capabilities to reduce petroleum hydrocarbons (PHC) in oily sludge. These include ultrasonic treatment alone, Fenton's reaction process alone, and the combination of ultrasound and Fenton's reaction (US/Fenton). Under the experimental conditions, the ultrasonic treatment and Fenton's reaction process achieved a reduction of 22.6% and 13.8% in the total petroleum hydrocarbons (TPH), respectively. However, a TPH reduction of 43.1% was observed for the combined process of ultrasound and Fenton's reaction, indicating that the individual AOP is complementary to one another. As a result, the combined process could be acted as a more effective method to treat oily sludge as compared to the single AOP.

Keywords: Fenton's reaction; oily sludge; oxidation; petroleum hydrocarbons; ultrasound

1. Introduction

Oily sludge is one of the major wastes generated from petroleum industry. It typically contains about 30-50% oil, 30-50% water, and 10-12% solids by mass [1]. Due to the existence of many recalcitrant heavy petroleum hydrocarbons (PHC) (e.g., long-chain alkanes and alkenes, polycyclic aromatic hydrocarbons), the remediation of oily sludge is of great difficulty. One potential method to destruct recalcitrant materials is the application of advanced oxidation process (AOP) [2]. During the AOP treatment, a large amount of hydroxyl radicals (·OH) with strong capability to oxidize organic pollutants can be generated. Ultrasound has been regarded as a "green" AOP technology to remove contaminants without the generation of secondary pollution [3]. It can generate ·OH radicals due to the acoustic cavitation that involves the formation and subsequent expansion of microbubbles under the periodic

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pressure variations [3]. Many studies have reported the effect of ultrasonic irradiation on the removal of organic compounds. For example, Torres et al. [2] found that the bisphenol-A concentration was under detection limit after treatment with ultrasonic irradiation (300 kHz and 80 W) for 90 min. Another AOP method is the use of Fenton's reagents (hydrogen peroxide H_2O_2 and iron) [4]. During Fenton's reaction process, a large amount of ·OH radicals can be generated simultaneously if the H_2O_2 approaches to Fe^{2+} ion. For example, Masomboon et al. [5] reported that a nearly complete removal of 2,6-dimethylaniline could be obtained in 4 h of electro-Fenton treatment under a pH value of 2, a Fe^{2+} concentration of 1 mM, and a H_2O_2 concentration of 20 mM. Villa et al. [6] also evaluated the effect of Fenton's reaction process on the degradation of DDT and diesel in soil, and they observed that 80% of diesel and 75% of DDT present in contaminated soil were removed after 64 h of Fenton's reaction.

The AOP efficiency can be affected by two aspects, including the production rate of free radicals and the extent of the produced radicals contacting contaminant molecules. The application of individual AOP might not be able to achieve high degradation efficiency and good economics. For example, it was found that the oxidation rates were relatively low when using ultrasound alone for the oxidation of chemicals [7]. In general, similar pollutant oxidation mechanism exists among various AOPs, and the individual AOP might be complementary to one another. As a result, the combination of different AOPs could achieve a better effect. For example, Virkutyte et al [7] investigated the effect of sono-Fenton-like process on the degradation of naphthalene, and they observed that the optimal degradation efficiency of naphthalene reached 97% when 600 mg/L of H_2O_2 was added into the soil while the ultrasonic power was applied. Neppolian et al. [8] reported that the degradation rate of *para*-chlorobenzoic acid (*p*-CBA) was 7.3×10^{-3} min^{-1} when using a combined process of ultrasound and Fenton-like reactions as compared to the value of 4.5×10^{-3} min^{-1} when only using ultrasound. The previous AOP studies mainly focused on the degradation of individual contaminants, and few studies applied AOP process to treat a mixture of hazardous organic compounds like the oily sludge. The objective of this study is then to evaluate the degradation efficiency of different AOP processes for oily sludge treatment, including ultrasonic irradiation (US), Fenton's reaction, and the combined US and Fenton's reaction process. The results would provide a sound basis for developing an efficient method for oily sludge treatment.

2. Materials and Methods

2.1. Oily sludge and chemicals

The oily sludge was obtained from the crude oil tank bottom in an oil refinery plant in western Canada. The sludge was kept in a capped stainless-steel bucket at 4°C, and its characteristics are listed in Table 1. The sludge was very sticky and its viscosity was not available. The concentration of total petroleum hydrocarbons (TPH) in sludge was measured using GC analysis as described below. The content of metal element was measured with Inductively Coupled Plasma (ICP) based on the ASTM D5185 method [9], and the water content was measured using the ASTM D1744 method [10]. The solid content was calculated based on the contents of water and TPH in sludge. Dichloromethane (DCM) (>99%, HPLC) was used for sample extraction, and cyclohexane (>99%, HPLC) was used with DCM to rinse columns packed with silica gel. Toluene (>99%, HPLC) was used as a solvent for PHC samples for GC analysis. Hexadecane (nC16; >99% pure), nonadecane (nC19; >99% pure), tetratracon (nC34; >99% pure), and pentacontane (nC50) were purchased from Sigma and they were mixed in toluene as standard compounds for PHC and fractional analysis. Silica gel (purchased from Sigma) was activated at 105 ◦C for 12 h, and anhydrous sodium sulfate was dried at 400 ◦C for 12 h before use. $FeSO_4 \cdot 7H_2O$ (purchased from Sigma) and H_2O_2 (30% w/w) solution were used as Fenton's reagents.

Table 1. Characteristics of oily sludge.

Parameter	Concentration	Parameter	Concentration (mg/kg)
TPH (by mass)	61%	Barium	2,136
Water content (by mass)	24%	Iron	6,339
Solid content (by mass)	15%	Zinc	209
Sodium (mg/kg)	76	Copper	43
Potassium (mg/kg)	423	Lead	19
Magnesium (mg/kg)	432	Chromium	11
Aluminum (mg/kg)	999	Nickel	9
Calcium (mg/kg)	1,145		

2.2. Experiments on the oxidation of PHCs in oily sludge

Laboratory experiments were carried out to examine the effects of three AOP processes on oily sludge treatment, including ultrasonic irradiation alone, the Fenton's reaction alone, and the combination of ultrasound and Fenton's reaction. In terms of the ultrasonic (US) treatment alone, a Misonix Sonicator 3000 generator with an ultrasonic frequency of 20 kHz was used. 1 g of oily sludge was put into a 100 ml beaker with 25 ml of deionized (DI) water. The ultrasonic probe was then placed into the sludge/water system for ultrasonic oxidation. The ultrasonic power was fixed at 60 W and the treatment duration was set up as 1, 3, 5, and 8 min, respectively. In terms of the Fenton's reaction process (Fenton) alone, 1 g of sludge was put into a 100 ml beaker, and then 0.63 g of $FeSO_4 \cdot 7H_2O$ was added into the system. The volume of H_2O_2 added to the beaker was set at 5, 10, 15, and 20 ml, respectively. The total aqueous volume in the beaker was consistent with that for ultrasonic treatment. Therefore, the volume of DI water added varied according to the dosage of H_2O_2 solution consumed in samples during the Fenton's reaction process, and they were 20, 15, 10, and 5 ml, receptively. Due to violent oxidation reaction, H_2O_2 was gradually added into the system until reaching the specified volume by using a 1-ml pipette. The mixture in the beaker was manually stirred during the Fenton's reaction process. In terms of the combination of ultrasound and Fenton's reaction (US/Fenton), the treatment was also conducted in a 100 ml beaker. 1 g of oil sludge was added into the beaker with 10 ml of DI water and 0.63 g of $FeSO_4 \cdot 7H_2O$. The ultrasonic probe was then placed under the liquid for ultrasonic treatment with the power of 60 W. 15ml of H_2O_2 was added into the system at a rate of about 3 ml/min during the US/Fenton treatment for 5 min.

2.3. Sample extraction and PHC analysis

The sample in the beaker after AOP treatment was transferred into a 50 ml tube for centrifugation for 30 min at 5000 rpm to separate the solid from the liquid for further analysis of PHC within the two phases. After centrifugation, the supernatant was transferred into a separating funnel for liquid extraction, and the solid residue left in the centrifugation tube was used to extract the PHC of the solids. In terms of the liquid-liquid extraction, 15 ml of dichloromethane (DCM) was added into the separating funnel containing about 25 ml of supernatant, and the funnel was shaken manually. After equilibrium for 30 min, the upper layer was collected into a glass tube. Another 15 ml of DCM was added to the funnel for another liquid-liquid extraction, and such extraction was conducted for three times. In terms of the solid extraction, 10 ml of DCM was added into the 50-ml centrifugation tube containing solids at the bottom. The tube was placed on a mechanical shaker for 30 min of shaking at 120 rpm, and was then sent for

centrifugation at 5000 rpm for 15 min. The liquid was then transferred into a glass tube. Another 10 ml of DCM was added into the centrifugation tube for a second extraction, and such extraction was also conducted for three times. The collected extraction solution in the glass tube was sent to a silica gel column for cleanup to remove moisture, particulate, and unwanted polar organic compounds [11]. The cleaned extraction was reduced to about 1 ml by using a rotary evaporator.

Toluene was used as a solvent to transfer the concentrated extraction to a final volume of 12 ml in a 15-ml vial. 2 ml of this extraction solution was then transferred into a 2-ml vial for TPH analysis using a Varian CP-3800 Gas Chromatograph with flame ionization (GC-FID). The external standard method was used for the analysis. Decane (C10), hexadecane (C16), tetratriacontane (C34), and pentacontane (C50) were used as external standards to determine the concentration of TPH and PHC fractions [12], where Fraction 1 (F1), Fraction 2 (F2), Fraction 3 (F3) and Fraction 4 (F4) is defined as the group of petroleum hydrocarbons from C6 to C10, C10 to C16, C16 to C34, and C34 to C50, respectively. The GC analysis conditions were set up as: ZB-capillary column with 30 m × 0.25 mm ID and 0.25-μm film thickness; inject volume of 1 μL; injector and detector (FID) temperatures at 320 °C; carrier gas (helium) at a constant flow rate of 1.5 mL/min during analysis. The split-less injection mode was performed on the 1079 PTV injector and after 0.7 min the split mode was activated at split ratio of 10:1. The capillary column temperature was initially held at 50°C for 1 min, then ramped at 15.0 °C/min to 110 °C and further increased at 10.0 °C/min to 300 °C and then was held for 11 min. The TPH reduction rate (η) was used to analyze the AOP efficiency, based on the measured TPH mass in the system before and after AOP treatment (M_0 and M_A):

$$\eta = \frac{M_A - M_0}{M_0} \times 100\% \quad (1)$$

3. Results and Discussions

3.1. TPH reduction using ultrasonic treatment alone

Fig. 1 presents the TPH reduction result using ultrasonic treatment alone. The initial TPH mass in the system with 1 g of oily sludge was 431.5±11.4 mg. After ultrasonic treatment, the remaining TPH (i.e. the total TPH mass measured from both liquid and solid phases) ranged from 334.0±8.6 to 363.8±22.6 mg, with the highest TPH reduction rate being 22.6%. The TPH reduction slightly increased from < 20% to 22.6% when the ultrasonic treatment time increased from 1 min to 5 min. However, longer treatment duration than 5 min did not improve the ultrasonic performance, and the TPH reduction slightly decreased to 16.3% after 8 min of US treatment. It was reported that the thermal cracking due to the collapse of cavitation bubbles and the free radical reaction initiated by hydroxyl radicals were the two major mechanisms for the degradation of organic compounds using ultrasonic irradiation [3]. The cavitation bubbles filled with vapor and/or gas formed via ultrasound can violently collapse to form “hot spots” where the temperature and pressure can reach up to 5000 K and several hundred atmospheres [2, 8]. These could result in the thermal scission of carbon-carbon (C-C) bonds in heavy PHC molecules. Meanwhile, the hydroxyl radicals (OH•) can be formed inside the cavitation bubbles by water pyrolysis when these bubbles collapse intensely. These radicals can then be transferred to the bubble interface and bulk liquid and react with the organic compounds [2]. The PHCs in oily sludge usually contain a large number of carbon atoms, and they have low vapor pressure and low solubility. Most of such PHCs are difficult to permeate into the cavitation bubbles. Thus, the free radical reactions could occur near the interface of cavitation bubbles and more often in the bulk liquid where the heavy PHC compounds are

largely present. In this study, solid particles present in oily sludge can produce a heterogeneous system for ultrasonic treatment. The liquid microjects resulting from ultrasonic irradiation in such system could enhance the transport of hydroxyl radicals into the interface region and the bulk liquid [2, 8]. This would further facilitate the contact of OH• radicals with the petroleum hydrocarbons, and thus enhance the ultrasonic oxidation reactions.

3.2. TPH reduction using Fenton's reaction treatment alone

Fig. 2 presents the TPH reduction results when using the Fenton's reaction process alone. After this AOP treatment, the remaining TPH mass in the sample ranged from 372.7±11.9 to 379.6±36.4 mg, as compared to the initial TPH mass of 431.5±11.4 mg. It can be found that a relatively higher TPH reduction (i.e. 13.8%) was achieved with the H_2O_2 dosage of 15 ml and 20 ml, which are equivalent to 600 ml/L and 800 ml/L of 30% (w/w) H_2O_2 solution in the system. In this study, the amount of H_2O_2 added into the system was much more excessive than the amount required for the degradation of all of the PHCs. For example, the carbon atoms in PHCs were about 29 mmol for 1 g of oily sludge, indicating that it would require 29 mmol of H_2O_2 for its complete oxidation. However, 5 ml of H_2O_2 was corresponding to about 50 mmol of H_2O_2. As a result, further increase in the H_2O_2 dosage from 5 ml to 10 ml, 15 ml, and even 20 ml, did not result in any further improvement in the oxidation of PHC (Fig. 2).

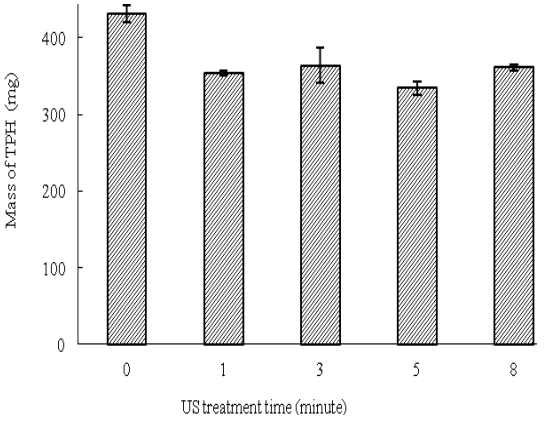

Fig. 1. Remaining TPH mass in samples after different ultrasonic treatment durations.

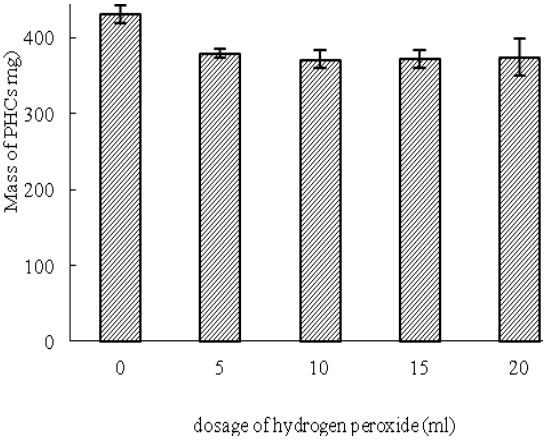

Fig. 2. Remaining TPH mass in samples after Fenton's reaction process alone.

The free hydroxyl radicals (OH•) have proved to be essential for the degradation of organic pollutants in the course of Fenton's reaction process. However, the TPH reduction in oily sludge through Fenton's oxidation alone in this study was relatively low. This may be explained by the inadequate contact of hydroxyl radicals with PHC. The majority of PHC in oily sludge was present in non-aqueous form or attached onto solid particles. These hydrophilic organic compounds were not able to thoroughly disperse into the aqueous phase during the Fenton's oxidation process, and thus it was difficult for the OH• radicals to attack substantial PHC molecules to achieve a high degree of PHC oxidation. However, the Fenton's reaction process is still a very attractive option to treat many organic compounds, especially for the recalcitrant compounds with complex structures. Hydroxyl radicals generated through Fenton's reaction process are strong and nonselective oxidants. The Fenton's reagents are relatively inexpensive

and the process is easily operated without any other energy requirement. Therefore, it is reasonable to combine conventional Fenton's reaction with other technologies to improve the radical-leading oxidation.

3.3. TPH reduction using combined ultrasound and Fenton's reaction process

A 5 min of ultrasonic treatment and a H_2O_2 dosage of 15 ml were selected for conducting experiments on the US/Fenton process based on the TPH reduction result of each individual method. Fig. 3 presents the remaining TPH mass in oily sludge samples treated by three AOP processes (US alone for 5 min, Fenton alone with 15 ml of H_2O_2, and US/Fenton with 5 min of ultrasound and 15 ml of H_2O_2). The TPH mass in the sample after US/Fenton treatment was 245.4±23.8 mg, which corresponds to a TPH reduction of 43.1%. This number is greater than the sum of the TPH reduction rates of US alone and Fenton's reaction alone, indicating a synergistic effect when combining US with Fenton's reaction process.

The reduction of individual PHC fraction in oily sludge after AOP treatment was also examined (Fig. 4). It can be found that the US alone and Fenton's reaction alone achieved a F2 fraction reduction of 23.7% and 29.6%, a F3 fraction reduction of 20.6% and 8.9%, and a F4 fraction reduction of 36.9% and 12.7%, respectively. The decomposition of long-chain hydrocarbons (i.e. F4 fraction) was more significant than the other two PHC fraction groups when using US treatment alone. This indicates that the release of ultrasonic energy can provide more convenient conditions for the cleavage of heavy PHCs. Meanwhile, the effect of Fenton's reaction on the degradation of F2 was more significant as compared with that for F3 and F4 fractions, indicating that the lighter PHCs can be more easily decomposed under the attack of OH• radicals. Combining US and Fenton's reaction process appeared to improve TPH reduction, and it achieved the highest PHC fraction reduction, with a reduction of 56.7%, 39.1%, and 46.5% being observed for F2, F3, and F4 fractions, respectively. The reduction rate for F3 fraction was less than that for F4 fraction. This might be attributed to the accumulation into F3 fraction due to the intermediate products resulted from the decomposition of heavy F4 fraction.

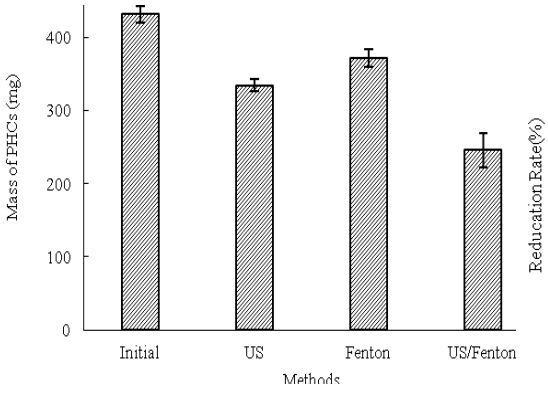

Fig. 3. Remaining TPH mass in samples using three different AOP methods.

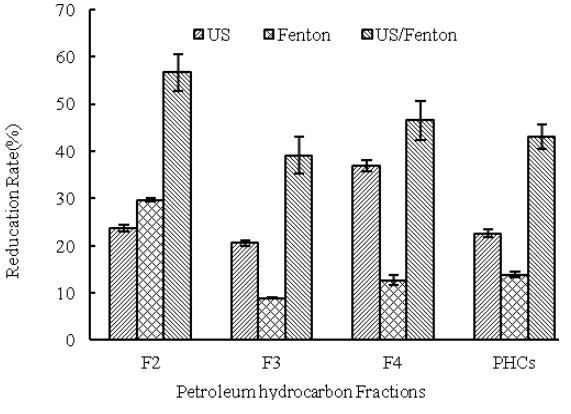

Fig. 4. Reduction of PHC fraction using three different AOP processes.

3.4. Distribution of PHC fractions after AOP treatment

Fig. 5 presents the distribution of petroleum hydrocarbon fractions in samples before and after three AOP processes. The samples with the highest TPH reduction rate under each AOP process were chosen

for comparison. It can be found that different distribution of PHC fractions exists after oxidation treatments. For example, after the US/Fenton treatment, the percentage of PHC fraction decreased from 21.72% to 16.71% for F2 fraction, and from 8.82% to 7.89% for F4 fraction, but increased from 69.46% to 74.28% for F3 fraction. Similar patterns were observed in the samples after Fenton's reaction treatment. Meanwhile, for samples treated with ultrasound alone, the percentage of F2 fraction was 21.96% as compared with the value of 21.72% in the original oily sludge sample. The percentage of PHC fraction increased from 69.46% to 71.42% for F3 fraction, but decreased from 8.82% to 6.62% for F4 fraction. The observation of increase in the percentage of F3 for all the samples implies the accumulation of by-products due to the oxidation/decomposition of F4 hydrocarbons. However, the structures of oxidation products after AOP treatments would be different from those in the original oily sludge. The carboxyl acid might be formed as the main by-products. The alkanes and branched alkanes would also be oxidized into ketones and alcohols with less carbon numbers. Further study should be conducted to investigate the composition of oxidation products after AOP treatment.

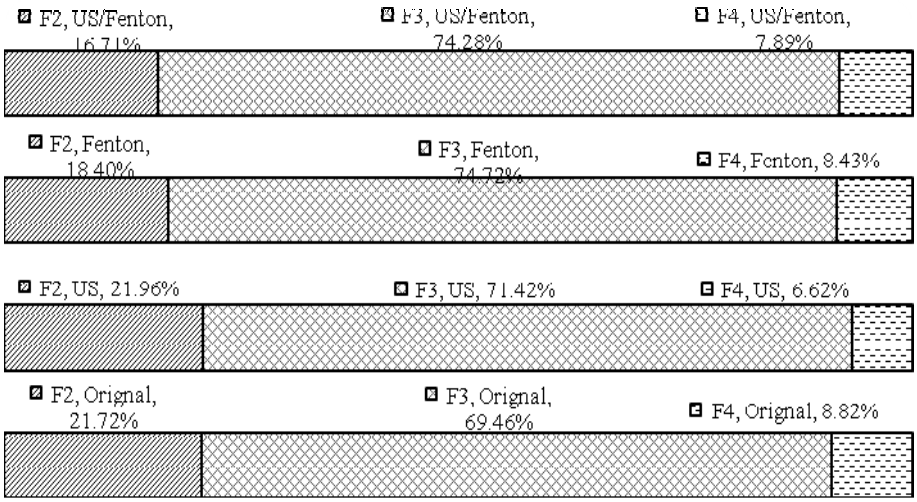

Fig. 5. Fractional distribution of petroleum hydrocarbons in samples before and after three different AOP processes (US alone for 5 min; Fenton's reaction alone with 15 ml of H_2O_2; US/Fenton with 5 min of ultrasound and 15 ml of H_2O_2).

4. Conclusion

Three advanced oxidation processes (AOP) were examined to treat oily sludge, a hazardous and recalcitrant waste in the petroleum industry. It was found that the TPH reduction in oily sludge reached 22.6%, 13.8%, and 43.1% when using ultrasonic irradiation alone, Fenton's reaction alone, and the combination of ultrasound with Fenton's reaction, respectively. For the combined process, the oxidation reaction in sludge system could be improved by increasing the contact of the hydroxyl radicals with petroleum hydrocarbons. The experimental results also revealed that the degradation of individual PHC fractions in oily sludge was greatly improved when using the combined process, with a reduction of 56.7%, 39.1%, and 46.5% being observed for F2, F3, and F4 fractions, respectively. As a result, the combined AOP process could be an effective way to treat the recalcitrant oily sludge.

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